# Directed Self-assembly with Density Multiplication of 6 tera-dot/in$^2$ Pattern by POSS-Containing Block Copolymer

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Directed self-assembly (DSA) of block copolymers (BCP) on chemically pre-patterned templates is perceived as a promising route to high density patterns with sub-lithographic resolution.[1] Previous studies have shown that, upon solvent annealing, strongly segregating BCPs containing polyhedral oligomeric silsesquioxane (POSS) can self-assemble into hexagonally closed packed (hcp) dot patterns of up to 4.6 tera-dot/in$^2$ (Tdpsi) with a 9× density multiplication.[2,3] In this study, we revert to thermal annealing of a lower molecular weight, $M_w$, POSS-containing BCP to further extend the density to ca. 6 Tdpsi.

Poly(methyl methacrylate-*b*-methacrylate POSS), PMMA$_{17}$-*b*-PMAPOSS$_9$, which self-assembles into a hcp array of dots with (10) lattice plane spacing $d_0$ = 9.7 nm, was synthesized by living anionic polymerization.[4] Sparse, chemically pre-patterned templates were prepared by electron beam lithography on a polystyrene layer grafted to a Si wafer. BCP thin films were spin-coated on the template with (10) lattice spacing, $d_{sub} = 3d_0$ = 29 nm. The samples were self-assembled by thermal annealing at 150°C or by solvent annealing in a neutral solvent atmosphere, namely a vapor of $CS_2$/acetone mixture, 9/1 (v/v).

Figure 1 shows a comparison of thermal vs solvent annealed thin films of PMMA$_{17}$-*b*-PMAPOSS$_9$ on both unpatterned and pre-patterned substrates. For films on a Si substrate, the thermally annealed sample (Fig. 1a) resulted in well-defined hcp crystallites with a relatively long lateral correlation length whereas the solvent annealed sample (Fig. 1b) exhibited a much shorter correlation length with a more disordered pattern. These results suggest that thermal annealing might be more appropriate for PMMA-*b*-PMAPOSS with low $M_w$ than solvent annealing. Similarly, for DSA on chemical contrast patterns, the thermally annealed film (Fig. 1c) showed a well-defined single crystal structure at 5.9 Tdpsi achieving a 9× density multiplication factor with respect to the chemical contrast pattern, while the solvent annealed sample (Fig. 1d) resulted in an imperfect pattern with no significant influence from the chemical contrast pattern.

For low $M_w$ PMMA$_{17}$-*b*-PMAPOSS$_9$ thermal annealing can achieve a longer correlation length than solvent annealing. On the other hand as we previously found, for larger $M_w$ (density ≤4.6 Tdpsi) it was achieved by solvent annealing.[3] Solvent annealing not only increases molecular diffusion, but it also depresses and shifts the effective interaction parameter. In the case of larger $M_w$, where the thermal diffusion of the BCP is limited and the segregation strength $\chi N$ is large, solvent annealing is appropriate to help with molecular diffusion without lowering $\chi_{eff}N$ near the order-disorder transition. On the other hand, in the case of lower $M_w$, the diffusion is larger and the $\chi N$ lower rendering the use of solvent annealing unnecessary as it may depress $\chi_{eff}N$ at or near the order-disorder transition producing patterns of poor quality. Under these conditions, thermal annealing results more advantageous to form well defined patterns at higher densities.

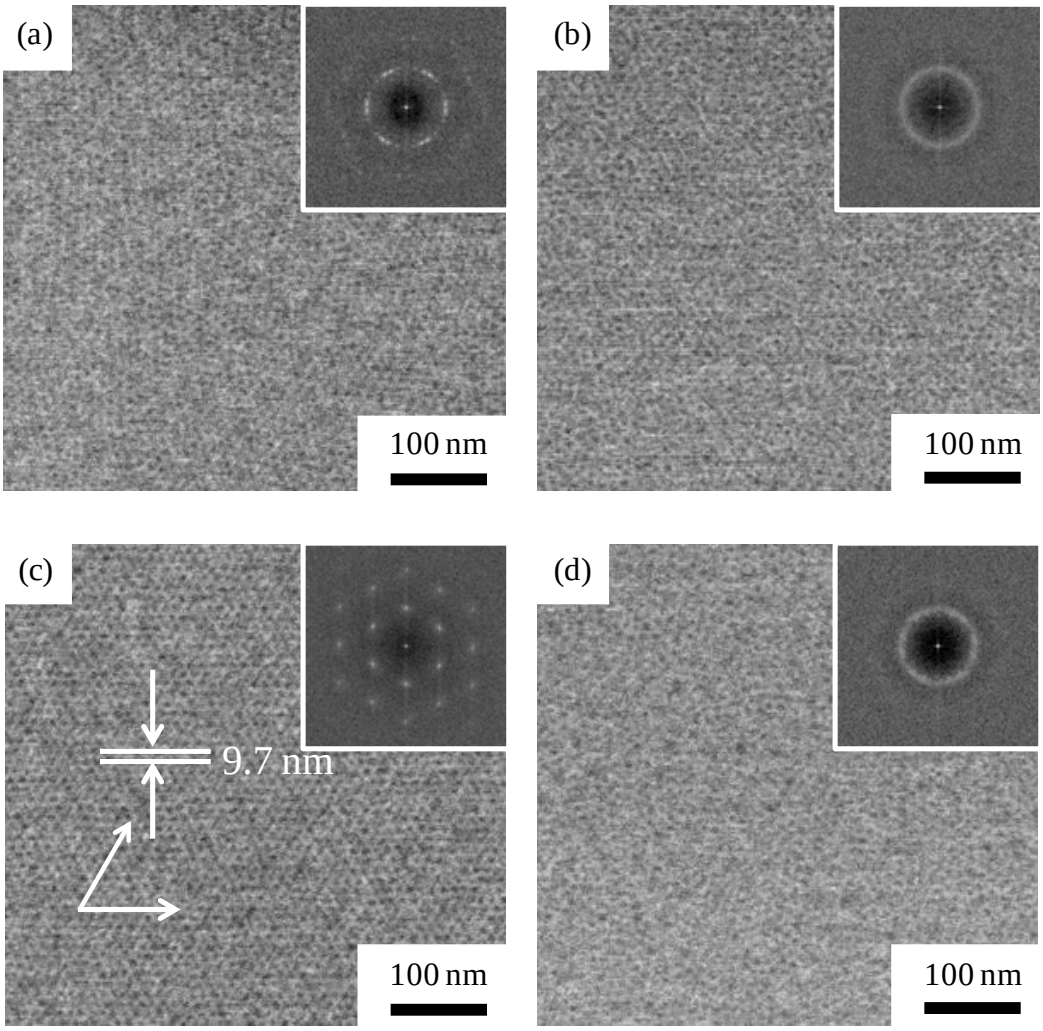


Figure 1. SEM and corresponding 2D-FFT images of $PMMA_{17}$-*b*-$PMAPOSS_9$ thin film self-assembled on an unpatterned Si substrate ((a), (b)) and chemically prepatterned template((c), (d)). (a), (c): annealed at 150°C for 48 h, (b), (d): annealed a vapor of $CS_2$/acetone = 9/1 v/v mixture for 2 hr at degree of swelling = 135 %.

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